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FREE RADICAL FORMATION DURING MACHINING AND FRACTURE
OF POLYMERS

by

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ABSTRACT

Electron paramagnetic resonance measurements of the number of free radicals formed during cutting and grinding of polymers are described. It was found in the semi-crystalline polymers studied that below the glassy transition temperature about 2×10^{13} free radicals are formed per sq cm of surface formed. It is proposed that this number results from the crack progressing selectively through the glassy regions about more ordered regions in the polymers.

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INTRODUCTION

Recently Eckert presented evidence that free radicals are formed during machining of polymers.⁽¹⁾ Electron paramagnetic resonance (EPR) measurements in our laboratory not only substantiate this observation but provide a quantitative measure of the number of free radicals present and, yields information about their identities.

EPR is a type of absorption spectroscopy that detects the presence of unpaired electrons resulting from ruptured covalent bonds such as those in polymer chains. The Varian E-3 used in these studies has a sensitivity of approximately 10^{11} to 10^{12} unpaired electrons under ideal conditions. This equipment has a TE₁₀₂ (rectangular) microwave cavity (2.29 cm height, 1.02 cm width, and 2.54 cm depth).

The sensitivity of this equipment is enhanced at low temperature approximately as the inverse of the absolute temperature. Also, free radicals, once formed, become very stable at liquid nitrogen temperature. Therefore, all spectra were recorded at low temperature even though the sample material was ground at various temperatures (room temperature $\pm 50^{\circ}\text{C}$) before quenching to liquid nitrogen temperature for storage and observation.

One might expect that machining, cutting, grinding, or other fracturing of many polymers should result in bond ruptures. For a random array of molecular chains with the density and molecular structure of Nylon 66, one would expect a plane passing through the cross-section of a sample to "cut" somewhat more than 2×10^{14} chains per cm^2 . A discussion of such calculations by Peterlin is found in ref. (2).

A comparison of the carbon-carbon bond energy (83 kcal/mole), giving rise to the tensile strength of the chain, with the secondary bond energy (3 to 6 kcal/mole), resulting in an interchain viscoelastic force, would lead one to expect chain segments of embedded material over about 100 carbon units in crystallites to rupture before "pulling out."⁽³⁾ Hence under proper conditions it should be possible to accumulate sufficient free radicals for detection by EPR techniques.

EXPERIMENTAL TECHNIQUE

As previously noted, a Varian Model E-3 EPR spectrometer was used in the present work. This equipment operates in the 8.8 to 9.6 GHz range and uses a field modulation of 100 kHz. Temperature control of the sample while the absorption spectrum was recorded was accomplished by a Varian E-4557/E-9540 variable temperature accessory. This accessory normally provides a sample space 4 mm diameter by 24 mm long. It was modified by the authors to provide a space 10 mm diameter by 24 mm long. This adaptation did result in a slight deterioration of the temperature maintaining capability of the accessory and an increase in temperature gradients. These were not, however, considered significant for the present studies and the modification allowed much more sample material to be present in the cavity thus generating much stronger signals.

The samples were prepared by slicing the end of strips of sample material in a specially prepared device. The resulting shavings were of the approximate dimensions of 1.1 cm x 0.15 cm x 0.07 cm. Approximately 50 such slices could be placed in the cavity. The slicing device consisted of a plane driven by a small dc electric motor as shown in Figure 1. A jet of dry pure nitrogen carried the newly formed slice through a tube where it was quenched in liquid nitrogen within one-half second of slicing. It was found that the sample material once quenched could be kept at least a week at these temperatures with no detectable decrease in free radical concentration. The temperature and atmosphere at which the slices were formed was controlled by placing the entire slicing device in a double-walled glass container (Figure 2). The space between the walls was evacuated, thus minimizing heat losses. The present studies were made

in a dry nitrogen atmosphere because oxygen exposure results in the development of peroxy signals and rapid decay of the concentration of free radicals.⁽⁶⁾ In these studies the temperature was varied from -30°C to $+110^{\circ}\text{C}$.

Sample materials included commercial grades of Nylon 66, polyethylene, and polypropylene, all in sheet form. Hot melt extrusion was used to form the sheets. The sheets were purchased in 0.050" thicknesses and cut to size for the slicing apparatus. The nylon was DuPont Zytel 101 and the extrusion of the sample materials was by the Polymer Corporation, Polypenco Division. A series of tests on desiccated nylon (in silica gel) were made to see what if any effect moisture content might have.

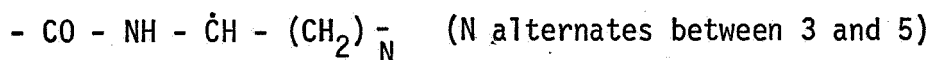
Nylon 66 was also ground with a small rotary file while submerged in liquid nitrogen. The grindings were studied under 50 power magnification on a metallograph. They were highly irregular in shape but typically had dimensions of the order of 10^{-3} to 10^{-1} mm. The surface area was measured on a Perkin-Elmer-Shell sorptometer and found to be 3000 to 7000 cm^2/gm . It should be noted that the sorptometer is most accurate in the range of surface areas of 100,000 cm^2 or more, resulting in this large variation.

There are two possible sources of error that are worthy of comment. The first is the reaction of new free radicals with oxygen or other species in the working atmosphere. Pure nitrogen was used but it is extremely difficult to keep it completely free of contamination. One source of contamination, for example, was the liquid nitrogen used as a quench. Inevitably it contained some oxygen which had been absorbed from the air during transportation and storage; some of it is likely to find its way into the slicing system. A second possible error relates to the type of reaction which might take place between free radicals and the metal they slide over for the short time after formation. There was a slight charge build-up on the metal. However, after establishing equilibrium, conservation of charge should restrict any further electron transfer. To date the authors have been unable to develop ways of quantitatively evaluating these sources of error. However, indirect evidence such as the consistency and reasonableness of the results indicate that the error from these sources is not extremely large.

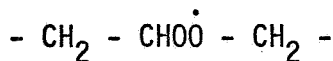
One other possible source of error is perhaps worthy of a few comments. Could it be that free radicals are formed in much larger concentrations than observed but part of them (for example, those right at the surface) have a lifetime much too short for observation by these techniques? A number of tests were conducted in an attempt to see if such were present. The most definitive of these was likely, careful and slow grinding of polymers at liquid nitrogen temperature. Studies of the signal strength immediately after grinding and after warming did not seem to indicate the presence of any such reactions. Such studies are not completely conclusive but gave us some confidence that the numbers measured probably do quite accurately represent the number broken.

RESULTS

Free radicals were observed in the sliced polymers. The nylon spectrum observed was very similar to the spectrum observed for the free radicals resulting from irradiation, grinding, and tensile loading.⁽⁴⁻⁷⁾ Its characteristic shape is attributed to the free radical being situated at the site



A typical spectrum for nylon sliced at 24°C is shown in Figure 3. Polypropylene and polyethylene are very susceptible to combining of their free radicals with oxygen and forming the peroxy radical. Consequently, the spectrum taken for these two were peroxy in nature. This must be attributed to the presence of traces of oxygen in the liquid nitrogen, evaporating into the system and causing a slight partial pressure of oxygen. For polyethylene the peroxy spectrum has been attributed to the free radical.⁽⁵⁾



It is relatively unimportant that a peroxy radical has formed since the number can still be determined. Our studies indicate that at the oxygen concentrations involved here the number of radicals before and after peroxy formation are the same within experimental error.

However, it is desirable to keep the concentration of oxygen in the slicing atmosphere small in order to reduce the rate of radical decay.⁽⁸⁾

The radicals observed by the spectrometer are in most cases not those formed directly by the rupture processes but rather secondary radicals formed from the original radicals by proton migration along the chain. More careful studies at very low temperature have isolated free radicals directly attributed to chain scission.⁽⁵⁾

By computer double integration of the recorded spectrum and a comparison of the resulting value with suitable standards the total number of "spins" could be determined.⁽⁹⁾ The total sliced surface area in the cavity was determined by counting the slices since all had the same dimensions. Free radical concentration based on the sliced or cut area was of the order of 10^{13} spins/cm². A very marked dependence on the temperature of the polymer during cutting was noted (Figures 4-6). For nylon the free radical density starts decreasing rapidly between 40 to 50°C which is close to the published glass transition temperature of approximately 50°C.⁽¹⁰⁾ Polypropylene on the other hand shows a decrease in the surface density at about 0° to 10°C and a published glass transition of -10°C.⁽¹⁰⁾ For polyethylene the temperature at which the free radical surface density begins to drop appears to be out of the temperature limits of the slicing apparatus. Polyethylene has a published glass transition temperature of about -125°C.⁽¹⁰⁾ It would appear that in each of the polymers tested the free radical surface density depends highly on the glass transition temperature of the polymer. Tests on desiccated nylon indicate that small amounts of water absorbed into polymer structures have little if any effect on the surface spin concentration. The sample material formed by grinding in liquid nitrogen is difficult to collect in large quantities; therefore, the surface area determination is relatively unprecise. The values obtained correspond to 7×10^{12} to 2×10^{14} spins for each square cm of new surface formed by the grinding.

Part of the pronounced decrease in free radical concentration above the glass transition temperature might be attributed to more rapid free radical decay at these temperatures. More studies of the kinetics of this decay at these temperatures must be made before exact figures can be given for this, but in light of the present studies it would appear that even at

the highest temperatures studied, free radical decay is not too significant in the short time between slicing and quenching.

DISCUSSION OF RESULTS

A number of interesting conclusions can be drawn from the above experimental results. A significant number of bonds are broken during cutting fracture in all the polymers studied. However, the number of bonds broken is considerably less than one might at first expect from the earlier arguments where it was stated that a plane passing through a cross-section would cut more than 10^{14} bonds per cm^2 . The actual number measured was down one order of magnitude from this. It would appear from these results that of the total surface energy required to form a new surface (determined by a crack or tear growth study to be of the order of 10^3 ergs/ cm^2 or more) the amount that can be attributed to primary bond rupture is only approximately 43 ergs/ cm^2 or a small fraction of the total.

We are of the opinion that the supposed discrepancies can be resolved in not too difficult a manner. The materials studied fall in the class of semi-crystalline polymers and are often portrayed as shown in Figure 7 with alternating regions of amorphous and crystalline material.⁽¹²⁾ A spherulite in nylon, for example, might be viewed as a sheaf or polycrystalline cluster consisting of a great many tiny single crystallites with intervening and interconnecting amorphous materials. Our studies would indicate that the crack surface then selectively chooses a path through this maze where less bonds need be ruptured than should it follow a plane. In the case of interest here it is apparently able to follow paths requiring less than one-tenth as many scissions as would be expected by a "cutting plane." A possible behavior for the Flory fringed micelle model is shown in Figure 8. While this particular model is perhaps rather outdated, it does, in common with most more recent models of the morphology of semi-crystalline polymers, portray the basic concept of regions of high crystallinity being surrounded by more amorphous regions.

The energy required to form a new surface during rupture must, as a consequence of the small amount that apparently goes into rupturing primary bonds, be largely that required to rupture secondary bonds and include plastic or viscoelastic deformation, somewhat analogous to the work of plastic deformation in front of a crack in metals.

It should perhaps be noted that based on different types of studies Peterlin et al have arrived at similar conclusions.⁽¹³⁻¹⁵⁾ Based on these observations we hypothesize that the fracture character and some other properties of semicrystalline polymers are strongly related to the regions between microcrystals and the number and character of the "tie chains" connecting these. These regions are drastically altered by drawing ratio, drawing temperature, etc.⁽¹³⁻¹⁵⁾ The large effect of drawing on strength (increases in tensile strength by an order of magnitude are common) is very likely largely dependent on these changes.

It would be of interest to know how the free radicals formed during rupture are distributed. Are all of the free radicals located at or very near the fracture surface, or are they more or less uniformly distributed throughout the volume, i.e. how localized is the damage? Since oxygen readily reacts with free radicals, studies of the kinetics of diffusion and reaction of oxygen on the cut or fractured sample should provide pertinent information the depth at which bonds are broken. Our results in this respect are as yet still very preliminary but would indicate that for the slicings more than 90% of the broken bonds lie within a couple of microns or so of the surface.

While the studies reported here relate to surfaces resulting from cutting and grinding operations, the conclusions might be much more general in their implications and should also apply to cases such as rupture during tensile fracture. Indeed one might expect that in the case of tensile fracture the crack might be even less restricted in following an "easy" fracture path with perhaps a further reduction in the number of broken bonds per cm^2 of crack. In the cutting operations the large stresses are restricted to a very localized region with the result that the crack might not always be able to progress along the easiest path. Other work in this laboratory as well as the work of Zhurkov and others^(5,11) have shown that EPR can indeed be used to study bond rupture during other types of mechanical rupture such as tensile fracture.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure

1. Photograph of apparatus used in preparation of the samples of sliced polymers.
2. The environmental chamber for the slicing apparatus.
3. A typical EPR spectrum of sliced Nylon 66.
4. The dependence of free radical surface density on fracture temperature of Nylon 66.
5. The dependence of free radical surface density on fracture temperature of polypropylene.
6. The dependence of free radical surface density on fracture temperature of polyethylene.
7. Fringed micelle model of semi-crystalline polymers after Flory (12).
8. Flory's fringed micelle model of a semi-crystalline polymer showing a selective fracture path.

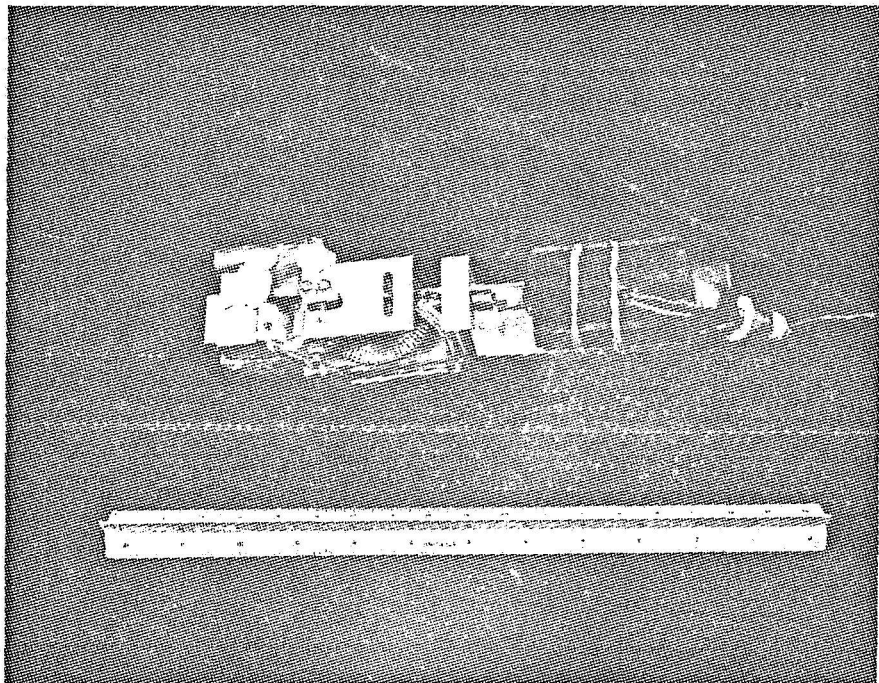


FIGURE 1

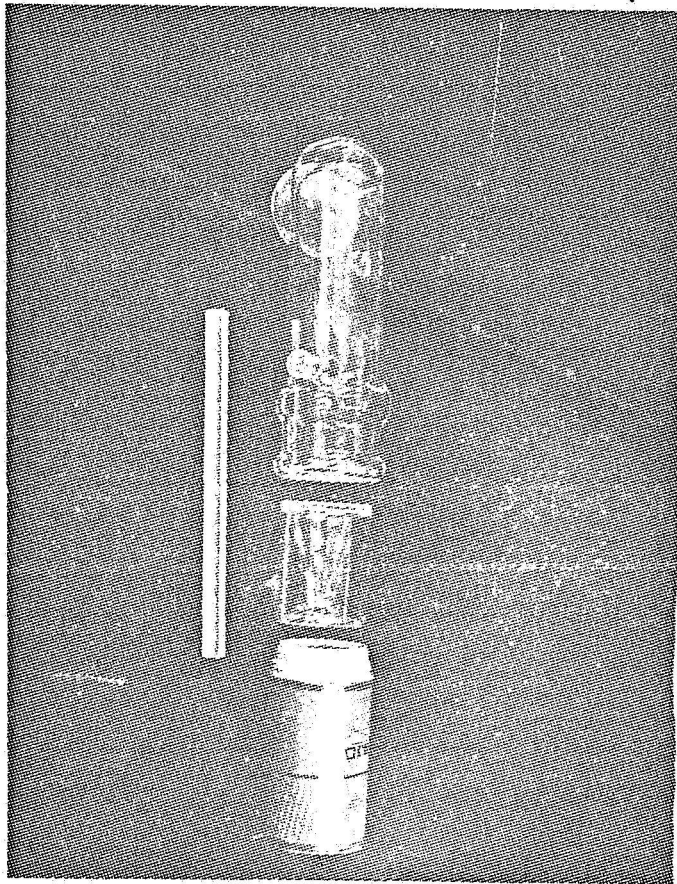
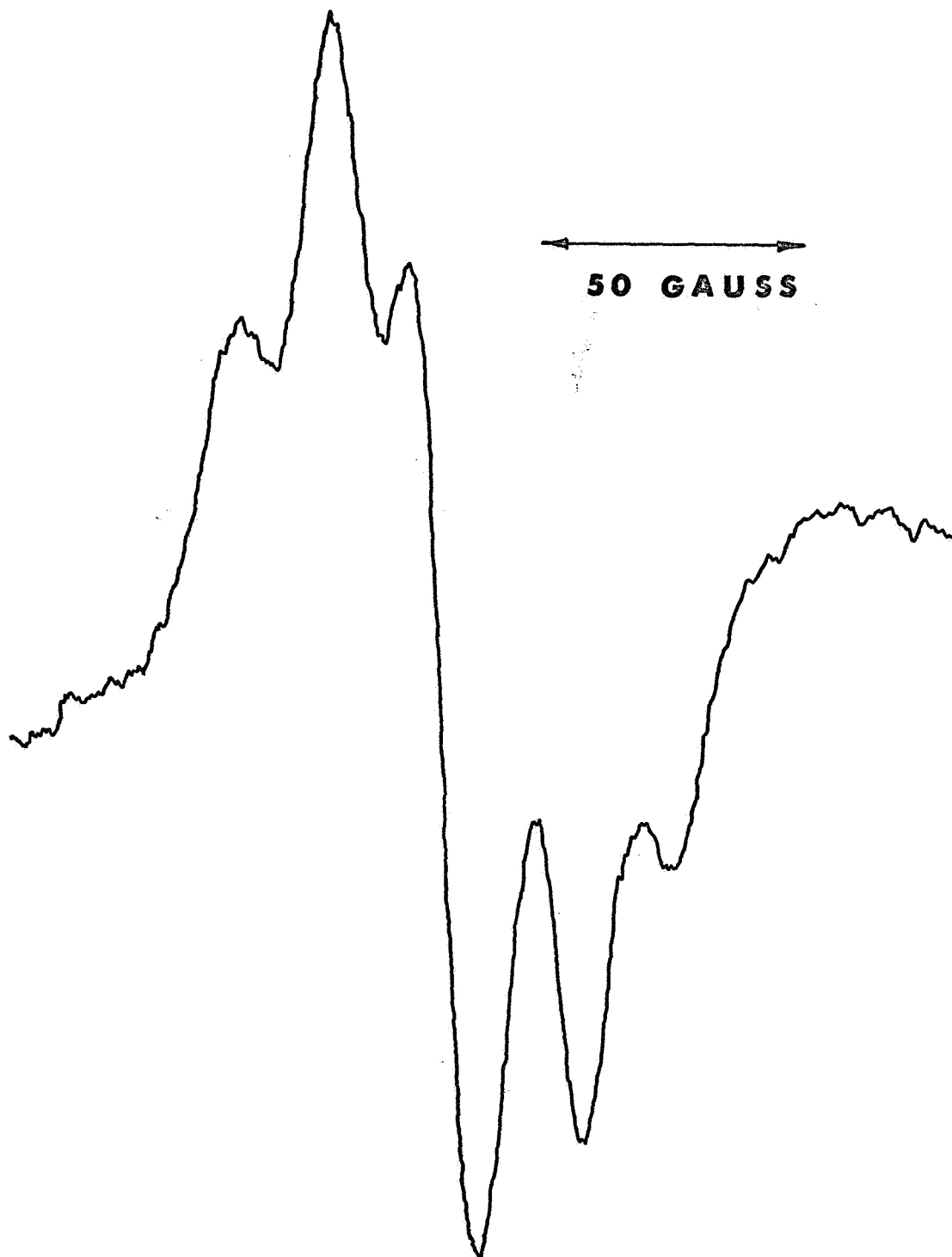


FIGURE 2



REDUCE (APPROX) TO
 $\frac{1}{4}$ SIZE
FIGURE #3

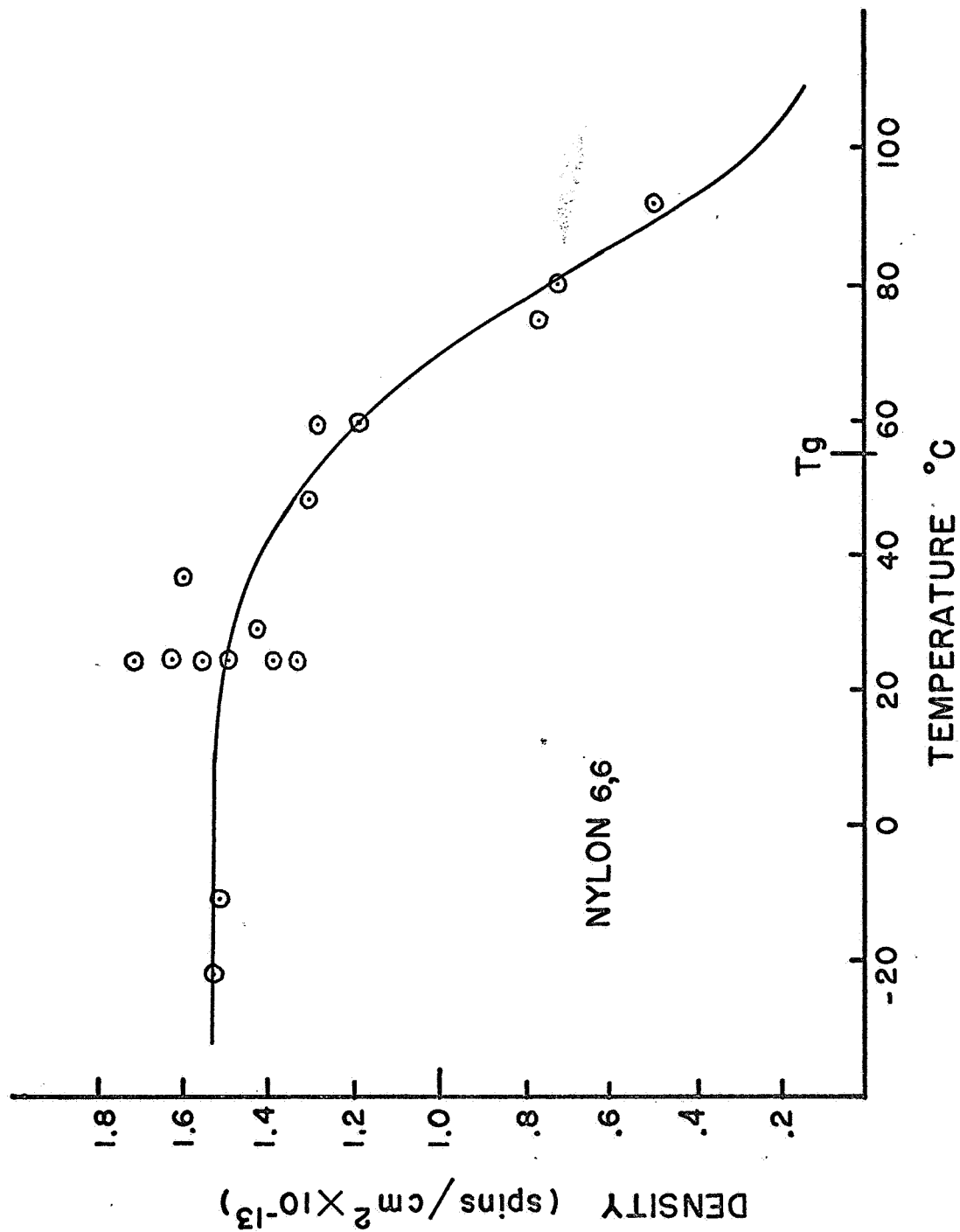


FIGURE A
REDUCED TO 1/2 SIZE

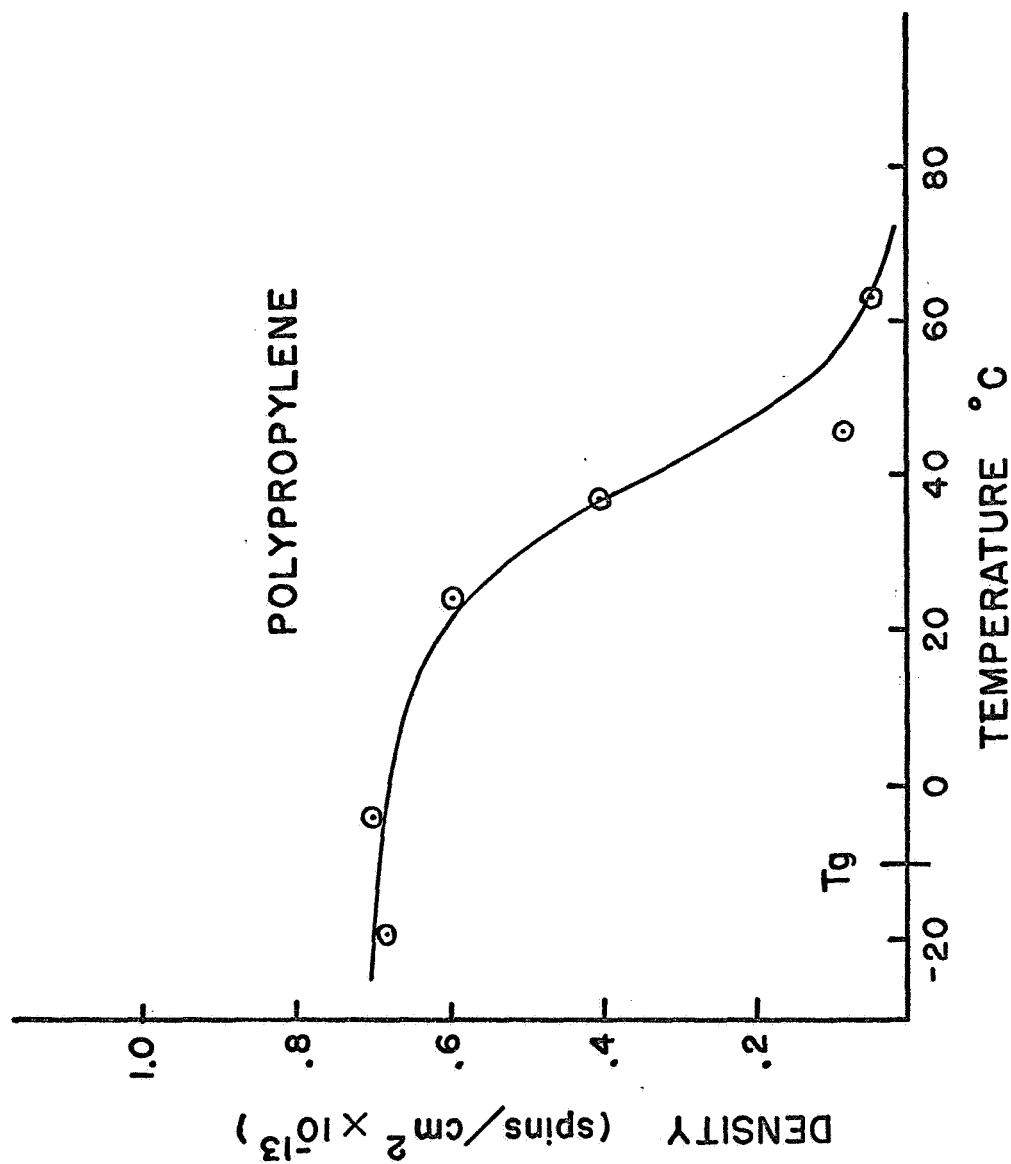


FIGURE 5
REDUCE TO 1/2 SIZE

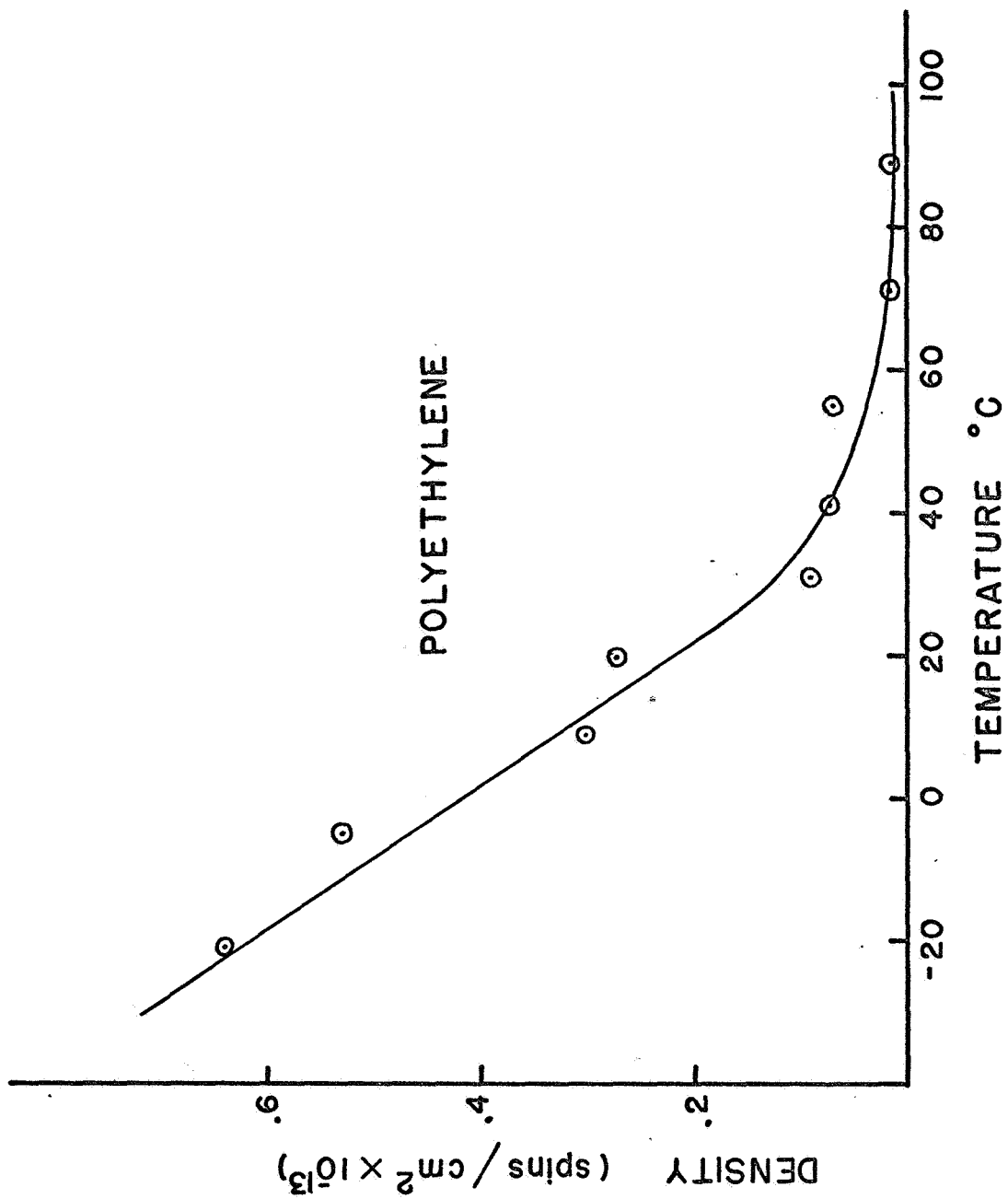


FIGURE 6
REDUCE TO 1/2 SIZE

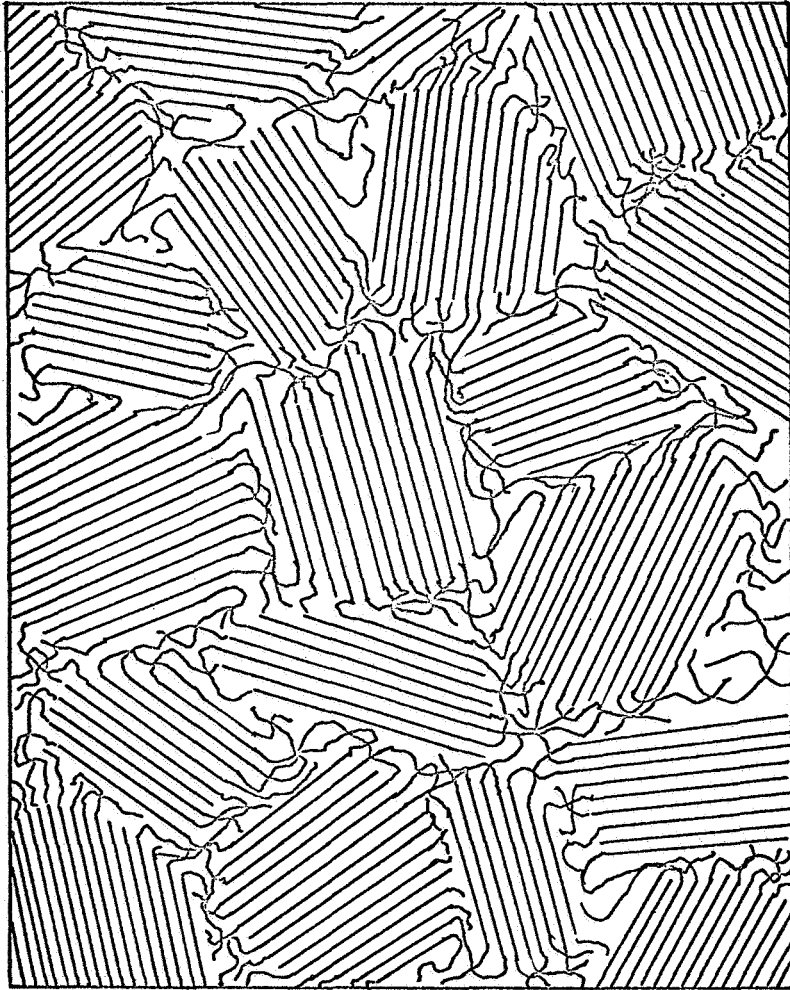


Figure 7



Figure 8